

COMPOUNDS OF METHYL SULPHIDE WITH HALIDES OF METALS.

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WHEN methyl sulphide is added to a solution of palladium dichloride a voluminous yellow precipitate is produced, which is apparently flocculent, but upon microscopic examination is seen to consist of very fine indistinct crystals.

If the liquid containing the precipitate is heated, the precipitate redissolves, giving a liquid of a bright orange color. On cooling, this solution deposits orange-colored needle-shaped crystals which may be washed and dried, apparently without change, and are stable in air and unaffected by light. The crystals are quite soluble in boiling water, but very slightly soluble in the cold.

An analysis of the crystals was made in the following manner:

A portion of the substance was dissolved in water and a current of carbon monoxide passed through the solution, which was kept upon a water-bath. Metallic palladium was precipitated. This was filtered through an asbestos filter, previously weighed. After drying, the metal was heated in a stream of hydrogen, and then, without admitting air, dry nitrogen was passed through the tube, and the metal finally allowed to cool in the stream of nitrogen. Experiments demonstrated that the finely divided palladium could be thus easily brought to constant weight. The nitrogen used was prepared from air by the use of alkaline pyrogallate to remove oxygen, and subsequent passage over a heated mixture of copper and copper oxide. The hydrogen chloride in the filtrate from the palladium was neutralized by zinc and the chlorine then determined volumetrically by silver nitrate solution.

The determination of sulphur presented difficulties. Many experiments were made in attempts to oxidize the sulphur of the compound to sulphuric acid by fusion with various mixtures of alkaline carbonate with nitrate and chlorate, and with sodium peroxide. All these experiments proved fruitless, as in every case a portion of the sulphur was lost by volatilization. Heating with nitric acid in a sealed tube, failed to yield complete oxidation, even at temperatures which involved danger to the tube. The ordinary reagents which might be looked to for the

conversion of sulphur into sulphuric acid, are of little use in the case of alkyl sulphides and their compounds. The most feasible method seemed to be by direct combustion in oxygen, and this was attempted in the following manner: The substance contained in a porcelain boat was placed in a porcelain combustion tube which was heated to a high temperature in a furnace. The front end of this tube passed through a cork in the neck of a nitrogen flask, containing a solution of sodium hypobromite. To permit of this mode of connection, it was necessary to place the furnace in a strongly inclined position. The products of the combustion passed through a roll of platinum gauze, 10 cm. long, rolled tightly, and completely filling the cross-section of the combustion tube. After passing the sodium hypobromite solution in the nitrogen flask, the products were led into a bottle of 7 liters' capacity containing a little bromine water. A soft cork, soaked in melted spermaceti, served to connect the side tube of the nitrogen flask with that leading into the large bottle. Thus rubber tube connections were wholly avoided. The sodium hypobromite solution together with the washings of the large bottle and combustion tube were acidulated, evaporated, and the sulphur determined by weighing as barium sulphate.

Experiments were tried also in heating the methyl sulphide compound in carefully purified hydrogen. The same apparatus and reagents were used as in case of the employment of oxygen, the hydrogen sulphide produced being then oxidized by the sodium hypobromite to sulphuric acid. There seems, however, to be some danger of dissociation of the hydrogen sulphide and possible deposition of sulphur in the colder parts of the combustion tube. Determinations by the methods described yielded the following results:

	Per cent.
Palladium	35.09
	35.19
Chlorine.....	23.75
	23.57
	23.65
Sulphur	21.57
	21.40
	21.41

The analytical results indicate for the compound the composition $\text{PdCl}_2 \cdot 2(\text{CH}_3)_2\text{S}$, the calculated percentages in the case of such a compound being:

	Per cent.
Palladium.....	35.41
Chlorine.....	23.46
Sulphur.....	21.22

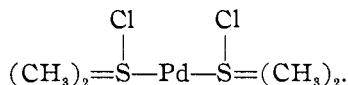
The above formula is similar to that given by Enebuske¹ to the compound of methyl sulphide with platinous chloride, $\text{PtCl}_2(\text{CH}_3)_2\text{S}$. The palladium chloride methyl sulphide is quite stable in solid form. In solution it is susceptible to the same changes as those undergone by palladium dichloride. In solution it is reduced by carbon monoxide and more slowly also by hydrogen. In the solid state it is reduced by hydrogen in the cold, with setting free of methyl sulphide and hydrogen chloride.

One hundred grams of water dissolved at 26.1°C ., 0.15 gram of the compound. The solution in water and also the dry substance possess a slight odor of methyl sulphide. It is soluble in a great number of organic liquids, including benzene, ether, alcohol, chloroform, acetone, ethylene dibromide, carbon disulphide, methyl iodide, commercial amylene, and gasoline. It fuses at 124°C ., solidifying again on cooling to a red crystalline mass. It seemed to be of interest to learn something of the products of its decomposition by heat. For this purpose, it was heated in nitrogen. At 210° an evolution of methyl sulphide began, and continued until the temperature rose to 260° , when a black residue was left, which proved on analysis to consist of nearly pure palladious sulphide. The gas escaping at the higher temperature, after being passed through water to remove any hydrogen chloride which might be present, was led through a glass tube containing sodium carbonate heated to redness. The sodium carbonate was afterwards tested and found to have absorbed chlorine. When the escaping gas was led through a solution of potassium hydrosulphide, methyl hydrosulphide was easily detected by its reactions toward ammoniacal solutions of silver nitrate and of copper sulphate. It was found that hydrogen chloride is not evolved on heating the compound. Hence, as chlorine had been found, and also the radical methyl, the compound methyl chloride was indicated. Moderately heated, therefore, the compound yields up a portion of its methyl sulphide. At a more intense heat it yields methyl chloride, palladium sulphide remaining as a residue.

As regards the constitution of the compound, it would seem

¹ *J. prakt. Chem.*, [2], 38, 358 (1855)

that the sulphur of the methyl sulphide might be tetravalent. The formula might possibly be written :



This is improbable, however, because the compound seems to contain chlorine linked with palladium, since hydrogen reduces the dry compound in the cold, just as it reduces dry palladium chloride, yielding hydrogen chloride in both cases.

It seemed to be of interest to study other compounds of methyl sulphide with halides of metals. The literature of the subject is scanty, little attention having been given to compounds of this class, since Loir¹ in 1853 described the compounds of methyl sulphide with mercuric chloride and iodide, and with platinic chloride.

For the preparation of the compounds described in this paper, it was necessary to obtain pure methyl sulphide. This was made by the method of Klason,² by distilling a mixture of sodium methyl sulphate with sodium sulphide.

COMPOUND OF METHYL SULPHIDE WITH MERCURIC CHLORIDE.

On adding methyl sulphide to a solution of mercuric chloride, a bulky precipitate of a white color is produced, which is seen under the microscope to be made up of indistinct crystalline needles. Exposed in a dry state to sunlight, the substance becomes somewhat darker in color. If preserved for some time in the solution in which it has been formed, it assumes a much more decidedly crystalline character. It is slightly soluble in water and more soluble in alcohol. The solution has a slight odor of methyl sulphide. It is slightly soluble in chloroform, carbon disulphide, ethylene dibromide, commercial amylene, benzene, acetone, and in petroleum gasoline. The solution in water yields a heavy yellow precipitate with caustic alkalies, and in other respects, the reactions in solution are similar to those of mercuric chloride.

Its melting-point varies with the rate of heating, as it undergoes partial decomposition, losing some of its methyl sulphide. When heated rather rapidly the lowest melting-point observed was 150°–151°, but if the heat is applied more slowly, its color

¹ *Ann. Chem. u. Pharm.*, **87**, 369 (1853); *Compt. rend.*, **34**, 1095.

² *Ber. d. chem. Ges.*, (1887), 3406.

grows darker, and as the result of a partial decomposition it melts at a varying and much higher temperature.

Heated in purified nitrogen it gives off methyl sulphide at about 150° , and at 170° white needle-shaped crystals form as a sublimate. No sulphide of mercury is formed as a result of heating. In the analysis of the compound the sulphur was determined by combustion in oxygen, as described in case of the palladium compound. Mercury was determined by precipitation of the aqueous solution by hydrogen sulphide and weighing as mercuric sulphide. Chlorine was determined by decomposition of the compound by zinc in presence of water and titration by silver nitrate solution. The results of the analysis are as follows:

	Per cent.
Mercury	64.27
	64.07
	64.19
Chlorine	22.26
	22.68
	22.66
Sulphur	6.63
	6.84
	6.76
	6.73

Other determinations were made in the case of the same compound after crystallizing from alcohol. The results were:

	Per cent.
Mercury	64.41
	64.31
Chlorine	22.60
	22.53

The calculated percentages in the case of a compound having the formula $3\text{HgCl}_2, 2(\text{CH}_3)_2\text{S}$ are as follows:

Mercury	64.63
Chlorine	22.70
Sulphur	6.42

Loir¹ assigns to the compound, obtained on adding methyl sulphide to mercuric chloride, the formula $\text{HgCl}_2(\text{CH}_3)_2\text{S}$. Analyses have been made of many preparations of the mercuric chloride methyl sulphide compound, but in no case has a product been obtained having the composition stated by Loir.

¹ *Loc. cit.*

COMPOUND OF METHYL SULPHIDE WITH CUPROUS CHLORIDE.

When methyl sulphide is added to a concentrated solution of cupric chloride, the color of the liquid changes from green to dark brown, and heat is evolved. After standing for a few hours, a mass of white crystalline scales forms at the bottom. The compound, if rapidly washed and dried, is white, but it is liable to turn to a yellowish green during drying. Exclusion of air does not serve completely to prevent this change of color. The crystals are almost insoluble in water, and are very slightly soluble in the various organic liquids mentioned in connection with the mercury compound. Boiling with water seems to expel part of the methyl sulphide. The substance dissolves in ammonia and in nitric acid.

Caustic alkalies decompose it, yielding an insoluble brownish red powder. Digestion of the substance with hydrogen sulphide, gradually changes it to copper sulphide. This reaction was made use of for a determination of the copper, the sulphide being ignited, redissolved, precipitated by sodium hydroxide, and weighed as cupric oxide. Chlorine was determined in the filtrate from the copper sulphide by the method already mentioned. As there seemed to be a possibility that the chlorine might be linked to carbon rather than to copper, and that consequently it might not be fully set free as hydrochloric acid in decomposing the compound by hydrogen sulphide, determinations were also made by heating the substance in a combustion tube traversed by a stream of hydrogen, absorption of the hydrogen chloride produced in water, neutralization by zinc and titration by silver nitrate solution. Determinations were also made by decomposition of the copper chloride compound by magnesium powder and titration of the chlorine as magnesium chloride. Sulphur was determined by the method of combustion in oxygen already described. The results of analysis were as follows :

	Per cent.	
Copper.....	39.12	
	39.13	
Chlorine.....	21.85	} Decomposition of the compound by hydrogen sulphide.
	21.80	
	21.76	} Decomposition by magnesium .
	21.77	
	21.76	} Decomposition by heating in hydrogen.
	21.60	
Sulphur.....	19.62	
	19.70	

The calculated percentages of the constituents named in the case of a compound having the composition $\text{CuCl}(\text{CH}_3)_2\text{S}$ are :

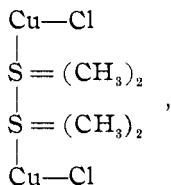
	Per cent.
Copper	39.46
Chlorine.....	22.00
Sulphur	19.90

Cuprous chloride methyl sulphide heated in nitrogen gives off methyl sulphide at about 100°C ., and continues to lose methyl sulphide until the temperature reaches about 200°C . After heating to a somewhat higher temperature the chlorine present in the residue in one experiment was found to amount to 21.53 per cent. of the original weight of the portion of the compound employed.

At a temperature above 400° the compound yields a mixture of copper sulphide and copper in wire form. The reaction occurring between methyl sulphide and the solution of cupric chloride which leads to the formation of the compound $\text{CuCl}(\text{CH}_3)_2\text{S}$, is characterized by great intensity as evidenced by the heat evolved and by the promptness of the change. One-half of the chlorine in the cupric chloride is eliminated and in its stead methyl sulphide becomes linked to the copper. Apparently, therefore, the substance resulting should be a cupric compound. Judged by its white color and its chemical properties it is, apparently, to be classed as a cuprous and not as a cupric compound. Yet it does not seem probable that the copper atoms can be in this case linked as is supposed to

be the case in cuprous chloride, $\begin{array}{c} \text{Cu—Cl} \\ | \\ \text{Cu—Cl} \end{array}$ The constitution of

the compound might perhaps be expressed by the formula



in which the sulphur appears to be tetravalent. The copper atom is no doubt linked more firmly to the chlorine than to the sulphur of the methyl sulphide. The question as to the classification of the compound as cuprous or cupric, seems to depend merely on whether there are one or two carbon atoms linked to

the copper atom. The linking of a chlorine atom, together with the sulphur atom of a methyl sulphide group to a copper atom, seems to impart to the compound a cuprous character as if the chlorine atom alone were present.

COMPOUND OF METHYL SULPHIDE WITH GOLD CHLORIDE.

When methyl sulphide is added to a solution of auric chloride, much heat is evolved, and an escape of hydrogen chloride occurs while an apparently flocculent white precipitate is produced. This precipitate is insoluble in water, but slightly soluble in alcohol. It may be washed and dried at room temperature by gas light. It is rapidly decomposed by sunlight, yielding metallic gold, methyl sulphide, and hydrogen chloride. If preserved in a dark place for a few weeks in the solution in which it was formed, and in presence of a slight excess of methyl sulphide, it assumes the shape of colorless crystalline needles.

It dissolves in various organic liquids, but the solutions soon deposit metallic gold. A determination of gold was made by exposing the substance under water to direct sunlight. The gold was rapidly reduced and was filtered out, burnt, and weighed in the metallic state. The chlorine was determined volumetrically in the filtrate from the gold. The sulphur was determined by combustion in oxygen, and weighing as barium sulphate.

The following analytical results were obtained :

	Per cent.
Gold	67.16
	66.98
	66.77
	67.42
Chlorine.....	12.32
	12.35
	11.97
	11.74
Sulphur.....	10.99
	10.88

These results suggest the composition $\text{Au} \begin{matrix} \diagup \text{Cl} \\ \diagdown \text{S}(\text{CH}_3)_2 \end{matrix}$, since calculation shows that such a compound would contain :

	Per cent.
Gold	66.90
Chlorine.....	12.02
Sulphur	10.87

The gold compound was heated in nitrogen, when it was found that an evolution of methyl sulphide begins at about 100° and continues until the temperature approaches 200° . At higher temperature, pure gold is left as a residue.

The reaction leading to the formation of the gold compound resembles that by which the copper compound is produced, in that the auric chloride undergoes reduction, and the aurous chloride then unites with methyl sulphide. A trivalent gold atom appears to have its affinities satisfied partly by a chlorine atom, and partly by the sulphur atom of a methyl sulphide group.

It seems that in the compounds which have been here mentioned the metal is more firmly linked to the halogen than to the sulphur of the methyl sulphide, and that the part played by the methyl sulphide is somewhat like that of water in various hydrated salts. Ferrous chloride remains a ferrous compound no matter what may be the number of water molecules with which it combines.

Hydrated magnesium chloride is well known to lose hydrochloric acid on strong heating and in a somewhat analogous fashion some of the compounds of metallic halides with methyl sulphide decompose on heating into metallic sulphide and methyl chloride.

A further study of compounds of alkyl sulphide with other metallic halides is in hand.

My acknowledgments are due to Mr. J. C. Fetterman, assistant in this laboratory, for his skill and careful attention to details in conducting many difficult and somewhat tedious analyses in connection with this work.

A NEW METHOD FOR THE ESTIMATION OF SOLUBLE NITROCELLULOSE IN GUNCOTTON AND SMOKELESS POWDER.

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A SHORT review of the methods now in use for the estimation of soluble nitrocellulose in guncotton and smokeless powder may be of interest to those who are not familiar with the subject under consideration. For this reason a brief description will be given here of the two methods most generally in use; namely, the (so-called) aliquot method, and the residual method which is